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Notice in accordance with Art. 7, § 1, Par. 2, No. 1 of the Law of 4 September 1967 (BGBl. I, p. 960): —

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Process for Preparing Stable, Fine-crystalline Structures in Solid, Partially Crystalline Polyolefins ---

The invention relates to a process for preparing stable, fine-crystalline structures in solid, partially crystalline polyolefins.

The degree of crystallinity of partially crystalline polyolefins is not a material constant, but largely a function of the thermal pretreatment of this high polymer.

A high degree of crystallinity is desirable in many fields of application in technology, because as the crystalline content increases, important mechanical and mechanical/thermal properties are increased and the dielectric strength improved.

The supermolecular state of order in the polymer influences its material properties far more than does the absolute degree of crystallinity. During cooling of the partially crystalline, molten high polymer, crystallites form initially, which combine into superstructures, so-called spherulites. The arising spherulites are not uniform formations in themselves. With slow cooling of the polymer melt, large, well-formed spherulites are obtained, particularly with linear, i.e., slightly branched polyolefins, whereas with rapid cooling small spherulites with an irregular crystal structure form. The formation of different supermolecular structures as a function of the thermal pretreatment is an important factor, which largely determines the macroscopic polymer properties.

It is known that a coarse-crystalline structure is more brittle and more susceptible to stress crack formation than a fine-crystalline material. For this reason, efforts are made in technology to obtain a fine-crystalline and homogeneous structure by skillful control of cooling during the

preparation process. During the manufacture of thin-walled articles (wall thickness ≤ 1 mm), this problem is not as critical as in the fabrication of thick-walled molded articles, where the selective cooling is limited by the poor thermal conductivity of the partially crystalline high polymer. Thus, a more or less nonuniform structure and thereby internal stress and shrinkage voids are obtained in these molded products or those with greater wall thickness differences due to nonuniform cooling over the entire cross section.

Such often unavoidable defects and nonhomogeneities in dielectrically stressed molded parts as well affect the electrical properties of the polymer very negatively. Mechanical and electrical properties accordingly depend very greatly on the previous processing history of the polymer. For this reason, a material with a stable, fine-crystalline structure is desirable, which is largely independent of the previous processing history.

It is prior in the art, in fact, to add inorganic substances, such as sodium sulfate, calcium chloride, silicon dioxide, silicates, and aluminum chloride, or organic salts, such as bismuth salicylate, aluminum succinate, aluminum-p-tert-butylbenzoate, and alkoxyaluminum benzoates, but also special monocarboxylic or polycarboxylic acids to polypropylene and other thermoplastics to obtain desirable properties such as increased transparency and stiffness. The mentioned compounds, however, have a few major disadvantages. Thus, they must be used in the form of very fine powders ($< 1 \mu$) or even in colloidal distribution in order to achieve the intended action. Furthermore, it must be stated that some of the previously known nucleating agents exhibit very different activity relative to the individual polyolefins. The good nucleating agent p-tert-butylbenzoic acid, known for crystalline polypropylene, exhibits no activity, e.g., in polybutene-1.

Tetrachlorophthalic anhydride in crystalline polypropylene increases the crystallization rate of the polymer melt and leads to a fine-crystalline structure. Pyromellitic dianhydride and phthalic anhydride, on the contrary, exhibit only minor activity.

Another disadvantage is that some of the known nucleating agents degrade important physical properties of the polyolefins. Even additives of an ionogenic nature or those with high dipole moment act especially negatively on the electrical properties. Mixtures of polyolefins with free carboxylic acids as nucleating agents can be processed only with difficulty, because the latter have the objectionable property of having a corrosive effect on the processing equipment.

Surprisingly, it has now been found that aromatic carboxylic imides and N-substituted aromatic carboxylic imides do not exhibit these disadvantages, and in partially crystalline polyolefin, preferably in low-density and high-density polyethylenes, partially crystalline polypropylenes, and polybutene-1, they produce fine-crystalline structures, which are less dependent on the previous processing history, with a simultaneously increased degree of crystallinity. The obtained fine-crystalline structures are thermally stable; i.e., no structural coarsening occurs in the microcrystalline solid at high working temperature ranges as well. A further advantage of the compounds of the invention is that they are thermally stable and easily dispersible in the polymer. Another advantage of the N-substituted aromatic carboxylic imides is that they have a small electric moment, and therefore are especially advantageous for polyolefins that are used in power and high-frequency engineering. The subject of the invention thereby is a process for producing stable, fine-crystalline structures in solid, crystalline polyolefins by addition of nucleating agents. The process is characterized in that 0.01 to 10% aromatic carboxylic imides and/or N-substituted aromatic carboxylic imides are used as an additive, based on the polyolefin weight.

The imides or N-substituted imides used as taught by the invention can be easily prepared from the corresponding aromatic dicarboxylic or tetracarboxylic acids and ammonia or aromatic and aliphatic amines. Suitable compounds are, e.g., naphthalimide, pyromellitic acid dianil, perylene tetracarboxylic acid dianil, naphthalanil, and N-anilinophthalimide.

Especially suitable are compounds that can be prepared from ring-halogenated dicarboxylic or tetracarboxylic acids and ammonia, aliphatic and aromatic amines, but preferably, ring-halogenated aromatic amines, therefore, e.g., tetrachlorophthalimide, N-(p-chloro)phenylphthalimide, tetrabromophthalanil, tetrachlorophthalanil, N-tert-butylphthalimide, N-n-butyltetrachlorophthalimide, N,N'-di-(p-chloro)phenylpyromellitic diimide, N-(p-chloro)phenyltetrachlorophthalimide, N-(2,4-dichloro)phenylphthalimide, N-(p-bromo)phenyltetrachlorophthalimide, and N-(p-chloro)phenylphthalimide.

Effective compounds according to the invention are also those in which the aromatic carboxylic acid and amine components contain alkyl and/or aryl substituents, therefore, substances such as e.g., N-phenyltetraphenylphthalimide, N-p-tolyltetrachlorophthalimide, and N-(p-chloro)phenyltetraphenylphthalimide. In partially crystalline polyolefins, the substances of the invention act as nucleating agents, which lead to the formation of very many and very small spherulites. The recrystallization of molten polyolefins nucleated with the substances of the invention begins at higher temperatures and the recrystallization process proceeds more rapidly and leads to a more uniform and finer crystal structure than without the addition these nucleating agents.

In so doing, it is not necessary to bring these substances to a particle size $\leq 1 \mu$. Advantageously, they can be used in particle sizes from 1 to 100 μ , preferably from 5 to 20 μ . The particular advantage of these substances is that they are highly active even at very low

concentrations. Amounts of 0.1 to 10%, preferably however 0.1–1%, based on the polyolefin, are sufficient to achieve the desired nucleating action.

According to the invention, the nucleating agents can be used in a mixture with one another and also with other known nucleating substances.

Crystalline olefin polymers, homopolymers, and mixed polymers of olefin polymers, preferably low-density and high-density polyethylene (density of 0.91–0.98), partially crystalline polypropylene, and polybutene-1 are suitable.

The aromatic carboxylic imides and substituted carboxylic imides used as taught by the invention are solid at room temperature and may be worked into the polyolefin by any conventional process, e.g., by blending the nucleating agent as a powder dry in a fluid mixer with the polymer or adding it to the polyolefin also dissolved in a suitable liquid or dispersed, and then processing the mixture in an extruder. Equally customary is the process of preparing a concentrate from the nucleating agent in the polymer, e.g., in a Banbury mixer, in an extruder, or on a roll in order to then add said concentrate to the pure polymer during the processing. The compounds used according to the invention can also be added directly to the polymer melt and incorporated into it.

The partially crystalline polyolefins with a stable, fine-crystalline structure obtained according to the process of the invention, which can be used particularly as molding compounds, may contain furthermore conventional additives such as aging stabilizers, light stabilizers, lubricants, high-melting waxes, dyes, or pigments.

Especially advantageous in carrying out the process of the invention are liquid, inert additives with a boiling point \geq the processing temperature of the polyolefin such as, e.g., aliphatic or aromatic hydrocarbons. They do not affect the microcrystalline structure formation, but slightly

slow down the crystallization rate of the nucleated material. As a result, the crystalline structure of the extruded or injection molded article can form over a slightly greater temperature interval, as a result of which the formation of internal stress is largely avoided.

The injection-molded articles, prepared from commercial isotactic polypropylene and the nucleating agents according to the invention at different mold and material temperatures, exhibit not only a higher degree of crystallinity (x-ray structure crystallinity) or a thereby synchronously greater density (buoyant density), but also a uniform, fine structure, primarily largely stable to processing conditions. By means of the higher crystallization temperature brought about simultaneously with the nucleating agents in the molding compounds, in association with a higher crystallization rate, there is a decisive advantage during processing, e.g., during injection molding, because the cycle time is shortened and thereby the ejection can occur within a shorter time.

Polymers prepared with the use of the nucleating agents of the invention, in comparison with polymers prepared with use of prior-art nucleating agents, exhibit not only a stable, micro-crystalline structure at an increased degree of crystallinity, but also improved mechanical and—in dielectrically stressed molded articles—also improved electrical properties. Because of the more uniform crystallization and the fine microstructure, the volume shrinkage proceeds much more uniformly during the cooling process, as a result of which shrinkage voids are largely avoided.

The crystallization temperature and the crystallization rate were determined with a hot-stage microscope under polarized light. To that end, a polymer sample, molded into a film, was heated to 200 °C on the hot stage and then cooled by 4 °C/min. The temperature at which the first

spherulites are visible was recorded as the recrystallization temperature, whereas the temperature at which the structure no longer changes optically was designated as the end of crystallization. The difference between the two temperatures (Δt) is a measure of the crystallization rate.

The invention will be illustrated in greater detail by means of the following examples.

Example 1

In a kneader, in each case 0.5% of the nucleating agents listed below is added to a commercial isotactic polypropylene, plasticized at 180 °C, (melt flow index i_5 of about 6) and processed into homogeneous mixtures. Each sample from the mixtures was molded into a film and examined on the hot stage of a polarization microscope, as described above. The Δt values, which were obtained with different mixtures and represent a measure of the crystallization rates, are summarized in Table I.

Table I

Isotactic polypropylene + nucleating agents (each 0.5%)	Δt value °C
Control material (without additive)	14.0
+ Tetraphenylphthalanil	5.0
+ Pyromellitic acid dianil	6.5
+ N,N'-Di-(p-chloro)phenylpyromellitic diimide	6.0
+ Perylene tetracarboxylic acid dianil	7.5
+ Naphthalanil	7.5
+ N-Cetyltetrachlorophthalimide	8.0
+ N-(p-chloro)phenyltetrachlorophthalimide	8.0
+ Tetrachlorophthalimide	8.0
+ N-Anilinotetrachlorophthalimide	9.0
+ Tetrachlorophthalanil	10.0

Example 2

In a kneader, in each case 0.5% of the nucleating agents listed below is added to a commercial isotactic polybutene-1, plasticized at 160 °C, (melt flow index i_5 of 0.5) and processed into homogeneous mixtures. Each sample from the mixtures was molded into a film and examined on the hot stage of a polarization microscope, as described above. The Δt values, which were obtained with different mixtures and represent a measure of the crystallization rates, are summarized in Table II.

Table II

Isotactic polybutene-(1) + nucleating agents (each 0.5%)	Δt value °C
Control material (without additive)	14.5
+ Pyromellitic acid dianil	5.0
+ Tetrachlorophthalanil	5.0
+ N-p-Chlorophenyltetrachlorophthalimide	8.0
+ N-Cetyltetrachlorophthalimide	10.0
+ Naphthalanil	10.0

Example 3

A mixture of commercial isotactic polypropylene (melt flow index is of about 6), prepared with an extruder, and 0.5% (based on the polymer) of pyromellitic acid dianil was injection molded on an injection molding machine into small standard test pieces (4 x 6 x 50 mm) at different cylinder and mold temperatures.

The molded articles were divided into small cubes with an approximately 1-mm edge length and the buoyant density (isopropanol/diethylene glycol) was determined. Table II shows the different test values. It shows not only the higher density values, due to the higher degree of crystallinity of the injection molded articles provided with pyromellitic acid dianil as the nucleating agent, but also that the variations in the density of the nucleated material are no longer as great as those of the control material, which undoubtedly indicates a more stable structure.

Table III

Density Values of Injection Molded Articles of Polypropylene (A)
and Polypropylene with 0.5% Pyromellitic Acid Dianil (B)

Injection molded articles		A g/cm ³	B g/cm ³
Cylinder temperature °C	Mold temperature °C		
210	30	0.9029	0.9054
230	30	0.9018	0.9047
250	30	0.9025	0.9047
270	30	0.9034	0.9050
210	70	0.9033	0.9059
230	70	0.9037	0.9054
250	70	0.9035	0.9056
270	70	0.9014	0.9051

Example 4

In a kneader, in each case 0.5% of the nucleating agents listed below is added to a commercial isotactic polypropylene, plasticized at 180 °C, (melt flow index i_5 of about 6) and processed into homogeneous mixtures.

A sample of the mixtures was pressed between two slides in each case at 200 °C (under an N_2 atmosphere) into very thin, small disks ($d \approx 100 \mu$) with a diameter of about 10 mm. The relative crystallinity of these samples was determined using a roentgenographic process. To that end, three diffractometer images were obtained for each preparation with CuK_α radiation (35 kV, 18 mA) with use of an Ar Geiger counter as a detector within the angle range $2\theta = 7$ to 31° always in the direction of higher angles of scatter. The images were evaluated by planimetry. The relative crystallinity X is established as a ratio of the area of the crystalline reflexes to the total area of the amorphous and crystalline scatter within the measured angle range.

$$X = \frac{P_k}{P_k + P_a}$$

Each image was evaluated repeatedly, and for each preparation from all measured values the average was determined, which is used as a measure of the relative crystallinity given in the following Table IV.

Table IV

Isotactic polypropylene + nucleating agents (0.5%)	Relative x-ray crystallinity
Control material (without additive)	0.56
+ Pyromellitic acid dianil	0.64
+ Tetrachlorophthalanil	0.62
+ Naphthalanil	0.65

6 claims

0 figures

Claims

1. Process for preparing stable, fine-crystalline structures in solid, partially crystalline polyolefins by addition of nucleating agents, characterized in that 0.01 to 10% of aromatic carboxylic imides and/or N-substituted aromatic carboxylic imides, based on the polyolefin weight, are used optionally in the mixture with other known nucleating substances.
2. Process according to claim 1, characterized in that 0.1 to 1% of a nucleating agent, based on the polyolefin weight, is used.
3. Process according to claims 1 and 2, characterized in that the nucleating agents have a particle size of 5 to 20 μ .
4. Process according to claims 1 through 3, characterized in that pyromellitic acid dianil is used as the nucleating agent.
5. Embodiment of the process according to any of the preceding claims, characterized in that the mixture to be processed is combined with an additive whose boiling point is greater than or equal to (\geq) the processing temperature of the polyolefin.
6. Process according to claim 5, characterized in that an aliphatic or aromatic hydrocarbon is used as the liquid additive.